



Short communication

Preparation of a trilayer separator and its application to lithium-ion batteries

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ARTICLE INFO

Article history:

Received 18 May 2010

Received in revised form 30 June 2010

Accepted 2 July 2010

Available online 13 July 2010

Keywords:

Inorganic separator
 Mechanical properties
 Lithium-ion battery
 Aluminum oxide

ABSTRACT

Inorganic particulate film/poly(methyl methacrylate) (PMMA)/inorganic particulate film trilayer separators are prepared by means of simple dip-coating of inorganic particle layers on to both sides of PMMA thin films. The mechanical, thermal and electrochemical characteristics of the trilayer are investigated using scanning electron microscopy, a universal tensile machine, a thermal shrinkage test and a charge–discharge test. As a polymer matrix, PMMA has exceptional compatibility with the carbonate-based liquid electrolyte, which can result in improved battery/cell performance. When inorganic Al_2O_3 particles are used to coat the PMMA film, drawbacks associated with gel-type membranes, namely, poor dimensional stability and thermal stability are greatly improved. This inorganic trilayer membrane is believed to be an inexpensive, novel separator for application in lithium-ion batteries.

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1. Introduction

Lithium-ion batteries have been attracting extensive interest from researchers who envision a growing market for energy storage for electric vehicles or fuel cell vehicles [1,2]. In the past few decades, many gel polymer electrolytes have been studied as candidates for improving the specific energy as well as the specific power of batteries [3–5]. High ionic conductivity of more than $10^{-3} \text{ S cm}^{-1}$ from gel polymer electrolytes has been obtained by adding a plasticizer and/or a polar solvent to a polymer matrix [6,7]. Several polymers have been used to form gel matrices, including poly(vinylidene fluoride)(PVDF), poly(acrylonitrile)(PAN), and poly(methyl methacrylate)(PMMA) [6–8]. It is difficult, however, to achieve high ionic conductivity without sacrificing dimensional stability which deteriorates when the content of polar solvent increases. Moreover, the melting points of most gel matrices are lower than 200°C and therefore can induce dimensional instability, which may cause internal short-circuiting or lead to thermal runaway. These drawbacks of gel polymer electrolytes hinder their application in large-scale applications.

Recently, separators made of inorganic sub-micron particles have been studied due to their excellent thermal stability and wettability with organic electrolytes. These particles require a substrate on to which they can be coated. That is, inorganic membranes themselves have insufficient mechanical strength to withstand the handling procedures used during cell winding assembly [9].

In this work, a novel trilayer separator is prepared with a PMMA layer coated with dense inorganic particles on both sides to obtain the synergistic effects from each layer [10]. This unique approach to the manufacture of trilayer separators overcomes the drawbacks of gel-type membranes, that include poor dimensional stability and thermal stability in the electrolyte saturation state.

2. Experiment

2.1. Preparation of inorganic particulate film/PMMA/inorganic particulate film membrane

The trilayer inorganic membranes were prepared as follows. First, 400 nm Al_2O_3 (Sumitomo Chem. Co.) powders were dispersed in xylene solvent (Aldrich) with a surfactant [3-(trimethoxysilyl) propylmethacrylate, Aldrich] and then heated at 130°C for 24 h. After the filtering process, the particles were washed with xylene and ethanol. The weighed Al_2O_3 powder and poly(vinylidene fluoride-co-hexafluoropropylene)(PVDF-HFP) (Kynar 2801, Arkema Co.) were dispersed in acetone and then ground for 3 h using a homogenizer. The typical composition ratio of the separator was 90:10 (by weight) Al_2O_3 :PVDF-HFP. PMMA (molecular weight of 350,000, Aldrich) was used as the polymer matrix, it was dissolved in N-1-methyl-2-pyrrolidone (NMP, Samchun Co. Ltd., Korea), and the solution was stirred to obtain a homogenous medium. The PMMA solution was, at first, cast on to a piece of glass plate by means of a surgical blade, and the solvent was evaporated at 80°C under vacuum for 10 h. After evaporation, a thin layer of PMMA was obtained by immersing the glass plate in distilled water. The membrane was further dried in a vacuum oven at 60°C . Then, the PMMA polymer matrix was dipped into the

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$\text{Al}_2\text{O}_3/\text{PVDF}$ -HFP solution for 1 s and dried in a chamber for 5 min (humidity 30%, temperature 20°C). Finally, the trilayer inorganic membranes were dried under atmospheric conditions for 24 h.

2.2. Preparation of electrodes

The anode had a composition of 94 wt.% graphitized mesocarbon microbeads (MCMB 2528) and 6 wt.% Kynar 741 as a polymeric binder. The cathode was composed of 90 wt.% LiCoO_2 , 6 wt.% Super-P, and 4 wt.% PVDF. The electrolyte for the bi-cell ($2\text{ cm} \times 2\text{ cm}$) was LiPF_6 (1 M) with ethylene carbonate (EC)/diethylene carbonate (DEC)/ethyl-methyl carbonate (EMC) (1:1:1 (v/v/v), Techno SEMICHEM Co., Ltd., Korea).

2.3. Physical and electrochemical measurements

The morphology of the trilayer inorganic membrane was examined by scanning electron microscopy (SEM, JSM-7000, Japan). To examine the thermal transition behaviour of the membrane, the samples were placed in an oven and heated at 150°C for 20 min. The mechanical properties of the separators were determined using a universal tensile machine (Nexygen Plus model LR30K tester, Lloyd Instruments, England). The test specimens were 6 mm wide and approximately $30\ \mu\text{m}$ thick, while the grip distance was 50 mm and the cross-head speed was 10 mm per min. For the charge–discharge test, a bi-cell with an electrode area of 4 cm^2 was used. Cells were charged up to 4.2 V at the 0.2C rate and were then discharged to 3.0 V at various C-rates. The charge process was cut off at 20% of the initial constant current.

3. Results and discussion

A schematic diagram of the proposed trilayer separator is presented in Fig. 1. The cross-section and surface morphologies of the trilayer separator as observed by SEM, are given in Fig. 2. The inorganic particulate films have porous structures due to the distance between the Al_2O_3 particles. The inner PMMA layer might have moderate ion conductivity due to a high electrolyte uptake without pores [11]. These structures have not only good thermal stability due to the inorganic materials but also high ionic conductivity that originates from the large uptake of the liquid electrolytes by the PMMA gel-type electrolyte. Moreover, the highly porous structures of the outer inorganic layers also contribute to high ionic conductivity.

In lithium-ion batteries, the essential role of the separator is to prevent electronic contact, while enabling ionic transport between the cathode and the anode. Thus, the separators should be stable in the battery for a long period of time at high temperature [1]. When the temperature rises to the softening temperature of the sepa-

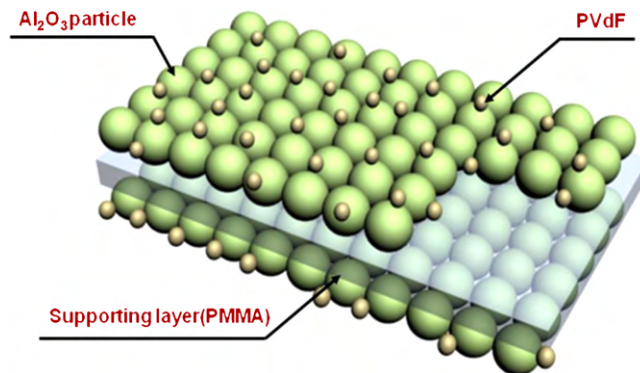


Fig. 1. Schematic diagram of organic/inorganic trilayer separator.

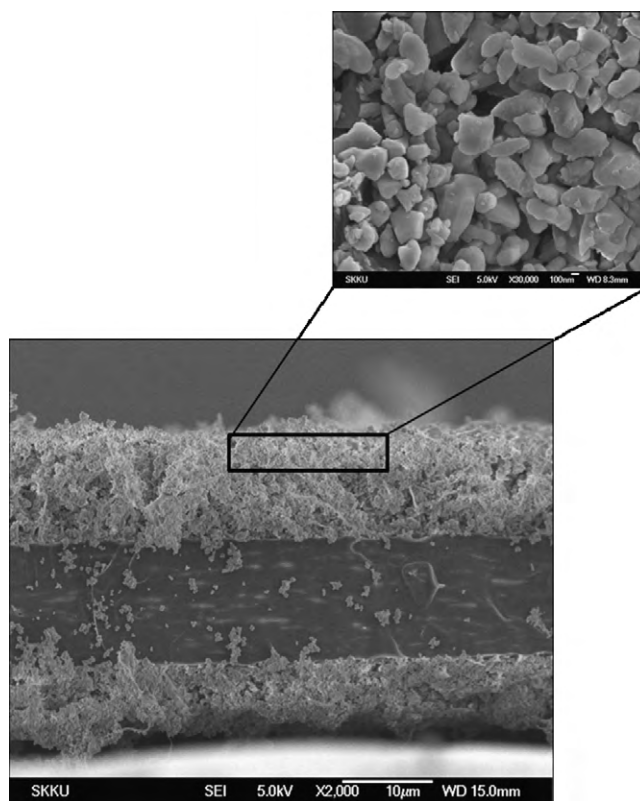


Fig. 2. Cross-section SEM of inorganic particulate film/PMMA/inorganic particulate film trilayer.

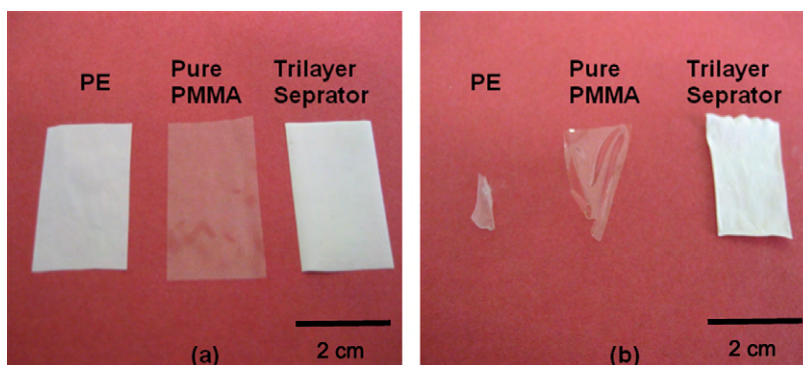


Fig. 3. Photographs of PE, pure PMMA and trilayer separator (a) before and (b) after being stored at 150°C for 20 min.

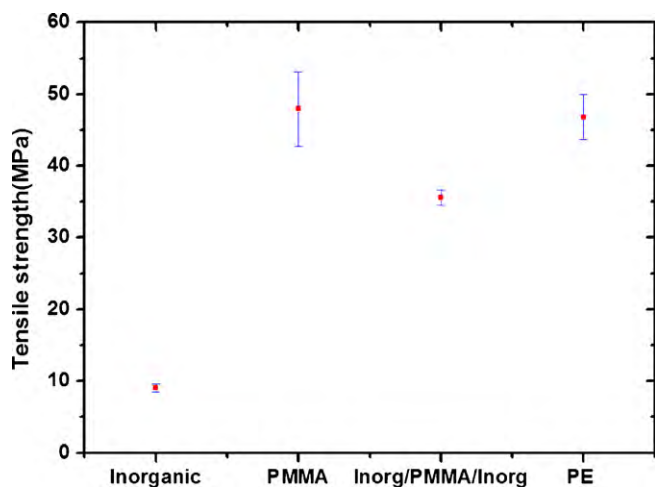


Fig. 4. Mechanical properties of inorganic, PMMA and inorganic/PMMA/inorganic separators.

rator material because of battery thermal runaway, conventional polyolefin-based separators tend to shrink due to internal stress [12]. In order to investigate the thermal-resistant characteristics of the trilayer separator, thermal shrinkage behaviour is observed after storing the separator at 150 °C for 20 min. Photographs of the PE separator, pure PMMA film and trilayer film membranes before and after storage at 150 °C for 20 min are given in Fig. 3. The photographs clearly show that the PE membrane and pure PMMA suffered a high degree of shrinkage during exposure to the high-temperature conditions. On the other hand, the trilayer separator undergoes the lowest degree of dimensional change.

The separator must be mechanically strong to withstand high tension during the battery assembly operation. The tensile strength of the inorganic trilayer separator compared with those of the PE and the pure PMMA films can be seen in Fig. 4. The mechanical strength of the inorganic particulate membrane itself is not acceptable for use in roll-to-roll processing. Even though the PMMA will be softened by absorbing a large amount of liquid electrolyte, the dried PMMA thin film has a tensile strength comparable with that of the PE separator. As shown in Fig. 4, the tensile strength of the inorganic separator is about 9.8 MPa. When PMMA is used as a polymer matrix, the tensile strength increases to more than three times that of a pure inorganic membrane. Based on these results, the enhancement in the mechanical strength of the inorganic trilayer separator is strongly influenced by the polymer matrix.

The separator itself does not participate in any cell reactions; but, its structure and properties considerably affect battery performance, including the specific energy, specific power densities and cycle-life. The used PMMA film should have a dense morphology because it is dried before immersing into water. Hence, the PMMA itself must be gelled by liquid electrolyte so that the necessary ionic conductivity can be obtained. When the PMMA film is 16 μm the liquid electrolyte uptake value is ~500%. The weight uptake of the PMMA film is calculated as follows.

$$\text{Weight uptake (\%)} = \frac{W_t - W_o}{W_o} \times 100 \quad (1)$$

where W_t and W_o are the weight of the wet and dry polymer membranes, respectively.

After the electrolyte uptake step, the PMMA has an ionic conductivity of $5.35 \times 10^4 \text{ S cm}^{-1}$ and this value is comparable with that of a commercialized PE separator ($3.43 \times 10^4 \text{ S cm}^{-1}$).

The rate characteristics of a lithium-ion battery were evaluated by charging the cell at a constant current of 0.2C and discharging it at various current densities, as shown in Fig. 5. The electrical

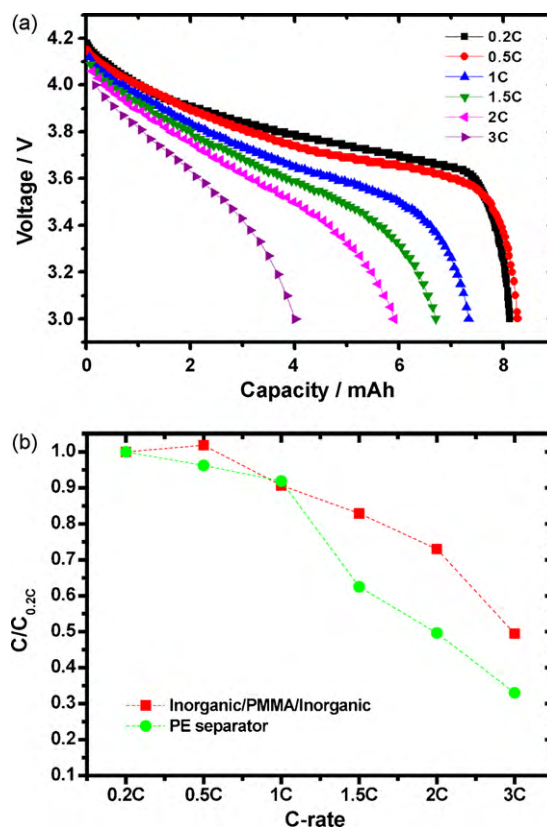


Fig. 5. (a) Discharge capacities of unit cell (anode+inorganic/PMMA/inorganic separator+cathode) at various discharge rates after charging at 0.2C, (b) comparison of rate performance of cells with PE separator and those with an inorganic/PMMA/inorganic separator at various discharge rates (ratio of capacities at various rates normalized against that at 0.2C).

polarization caused by the serial resistance increases as the current rate is increased and thereby results in a decrease in capacity. The reduced capacity at a high current rate is due to the lower diffusion rate of lithium ions into the separator. The relative capacity of the cell is plotted against the discharge current in order to compare the PE separator and inorganic trilayer separator. As shown in Fig. 5(b), the inorganic trilayer separator experiences less capacity drop at high discharge current densities. Because all other components in the cells are the same, except the separator, the enhanced power characteristics may originate from the highly porous structures of the outer layers as well as the high electrolyte uptake of the inner PMMA layer. In the case of the trilayer separator, the capacity at the 0.5C rate is slightly higher than that at the 0.2C rate. The crossover phenomenon is abnormal and could result from cell irregularity.

As reported previously, PMMA will melt at around 180 °C. Because the outer layers composed of inorganic particles have very high thermal stability at temperatures up to 500 °C, it is expected that the trilayer separators will show very high stability under abusive conditions. To confirm this hypothesis, further studies on the thermal stabilities of the unit cells and long-term stability tests are necessary.

4. Conclusions

An organic/inorganic trilayer membrane consisting of $\text{Al}_2\text{O}_3/\text{PMMA}/\text{Al}_2\text{O}_3$ has been prepared. The membrane shows not only exceptional thermal integrity due to the inorganic layers, but also enhanced mechanical properties due to the good tensile strength of the inner PMMA layer before the addition of liquid electrolyte. Lithium ion cell with the trilayer separator shows ade-

quate capacity retention with increasing C rate. The results show that this unique multilayer polymer membrane is a promising candidate for separator applications.

Acknowledgment

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government(MEST) (NRF-2009-C1AAA001-2009-0094157).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:[10.1016/j.jpowsour.2010.07.016](https://doi.org/10.1016/j.jpowsour.2010.07.016).

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